PATENT ABSTRACTS OF JAPAN
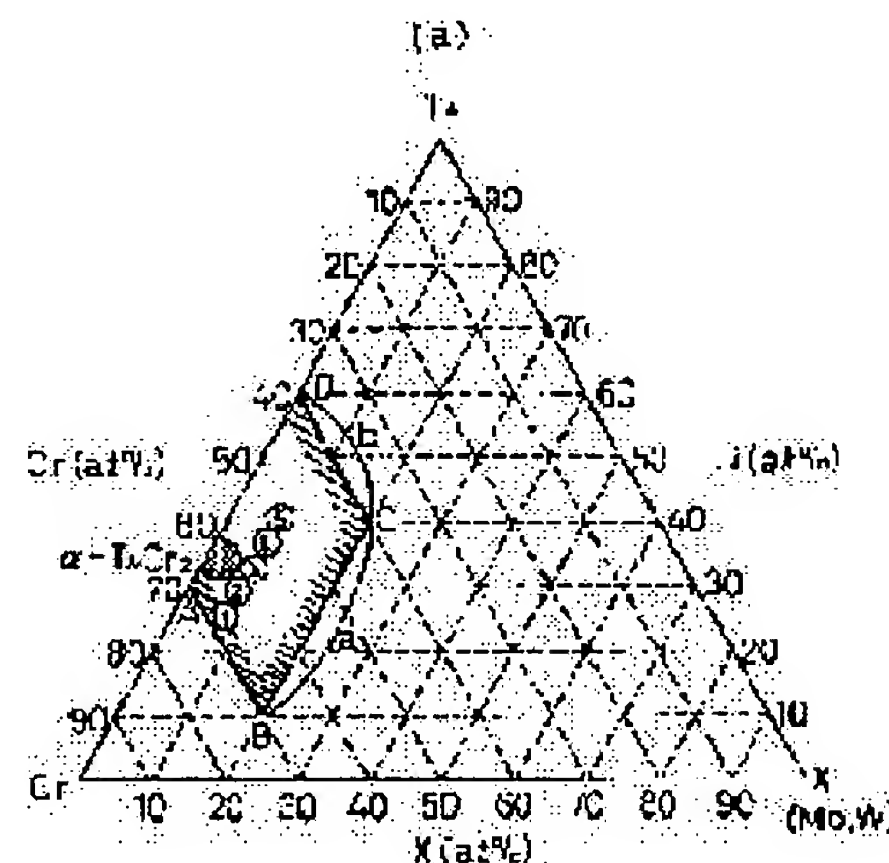
(54) HYDROGEN STORAGE ALLOY AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen storage alloy requiring no particular use of expensive alloying elements such as V, having a hydrogen absorbing and releasing capacity equal to that of the conventional BCC type hydrogen storage alloy, and advantageous in respect of manufacturing costs, and its production.

SOLUTION: The hydrogen storage alloy has a composition represented by formula $Ti_{100-a-b}Cr_aX_b$ [where X is at least either of Mo and W and the symbols (a) and (b) satisfy, by atomic %, $40 \leq a \leq 70$ and $0 < b \leq 20$, respectively]and also has a crystalline cubic structure composed of body-centered structure (BCC type). As the method of manufacture of this hydrogen storage alloy, the aforesaid alloy is melted and cast, and the resultant ingot is held at 1200-1400°C (excluding TiCr single phase region) for 1-5hr and then subjected to rapid cooling treatment, by which the crystalline structure is provided with body-centered cubic structure (BCC type) at ordinary temp.

	Ti	Cr	X
①	27	86	7
②	30	63	7
③	33	60	7
④	36	57	7
⑤	39	54	7

LEGAL STATUS

[Date of request for examination]

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CLAIMS

[Claim(s)]
[Claim 1] A presentation is the hydrogen storing metal alloy which general formula Ti100-a-b Cra Xb, however X are at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and is expressed with $40<=a<=70$ and $0< b<=20$, and is characterized by the crystal structure being body-centered cubic structure (BCC mold).

[Claim 2] The manufacture approach of the hydrogen storing metal alloy characterized by making as [have / the crystal structure / by holding the alloy of claim 1 after the dissolution / casting, holding this ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, TiCr2 except for a single phase field), and performing quenching processing after that / in ordinary temperature / body-centered cubic structure (BCC mold)].

[Translation done.]

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[Claim 2] The manufacture approach of the hydrogen storing metal alloy characterized by making as [have / the crystal structure / by holding the alloy of claim 1 after the dissolution / casting, holding this ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, $TiCr_2$ except for a single phase field), and performing quenching processing after that / in ordinary temperature / body-centered cubic structure (BCC mold)].

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Without using alloy elements, such as expensive V, especially about a hydrogen storing metal alloy, this invention has the hydrogen absorption/emission ability of the conventional BCC mold hydrogen storing metal alloy and this level, and relates to the advantageous hydrogen storing metal alloy in manufacturing cost, and its manufacture approach.
[0002]
[Description of the Prior Art] as a storage / transportation means of hydrogen, a hydrogen storing metal alloy carries out occlusion of the hydrogen gas of about 1000 times or more of the own volume of an alloy, and stores it -- possible -- the volume density -- a liquid or solid-state hydrogen -- almost -- an EQC -- or it is more than it. LaNi5 by which the metal of the body-centered cubic structure (Following BCC is called) of V, Nb, Ta, a TiVMn system, a TiVCr system alloy, etc., etc. is already put in practical use as this hydrogen absorption ingredient etc. -- AB5 mold alloy and TiMn2 etc. -- AB2 Compared with the mold alloy, carrying out occlusion of a lot of hydrogen was known for many years. This is because there are many hydrogen absorption sites in the crystal lattice and the hydrogen storage capacity by count is very as large as H/M=2.0 (alloys, such as Ti, V, etc. which are about 50 atomic weight, about 4.0 wt(s)%) with BCC structure.
[0003] Moreover, in a pure vanadium alloy, occlusion of the almost same about 4.0 wt(s)% as the value calculated from the crystal structure is carried out, and the abbreviation one half is emitted under ordinary temperature ordinary pressure. It is known that a big hydrogen storage capacity and a good hydrogen desorption property are similarly shown in 5A group's Nb and Ta of an element of the same periodic table. However, with pure metals, such as V, Nb, and Ta, since cost is very high, by the industrial application which needs a certain amount of amounts of alloys, such as a hydrogen tank and a nickel-MH cell, the property has been examined in the alloy of the component range which has BCC structures, such as Ti-V. Although the BCC mold hydrogen storing metal alloy which contains such Ti on the other hand is high capacity, since all contain expensive V, the hydrogen storing metal alloy which has the capacity of equivalent level, without including V to this can expect an epoch-making cost merit in the application which needs a high capacity hydrogen tank [for electric vehicle (EV)] hydrogen storing metal alloy.
[0004] Moreover, although V is eluted in the electrolytic solution in a nickel-MH cell, with the alloy which does not contain this, application to the negative-electrode material of a nickel-MH cell is also expectable. To JP,4-210446,A, a hydrogen storage capacity is increased with the comparatively cheap cost of materials, and it is arc-dissolution-indicated under the high grade Ar gas ambient atmosphere in the TiCrMo system and the TiCrMoFe system for the purpose of enlarging a reaction rate further as a well-known technique of this field being the amount of hydrogen absorption/emission in -40 degrees C and that the effectiveness of occlusion and emission and a reaction rate are further improvable. Moreover, to JP,61-176067,A, a kind of element chosen as a Ti-Cr alloy from alkaline earth metal etc. is added, and the hydrogen storing metal alloy for offering the long metal hydride electrode of the cycle life by charge and discharge is indicated.
[0005] However, in addition to the point of difficulty in activation that the reaction rate made into the problem in V system is slow, with these BCC alloys, new troubles, like there are few burst sizes only by carrying out occlusion by practical temperature and pressure are also produced. Consequently, the alloy which makes a BCC phase a main configuration phase has not yet resulted in practical use. Furthermore, development of the alloy in which did not contain expensive alloy elements, such as V, and the hydrogen absorption/emission property was excellent is desired.
[0006]
[Problem(s) to be Solved by the Invention] The purpose of this invention examines permuting V in the Ti-V-Mn system of the conventional BCC mold hydrogen storing metal alloy, and a Ti-V-Cr system alloy by Mo and/or W, and offers a cheap hydrogen storing metal alloy by high capacity. Moreover, it is advantageous in manufacturing cost and other purposes of this invention offer the hydrogen storing metal alloy which has the hydrogen absorption/emission

property whose application in a industrial scale is enabled as a hydrogen tank or an object for nickel-MH cells with said alloy excellent in the hydrogen absorption/emission property. Moreover, another purpose of this invention attains the optimal production process for enabling manufacture in a industrial scale by low cost with the above-mentioned new BCC alloy by the heat treatment approach.

[0007]

[Means for Solving the Problem] As for the above-mentioned purpose, the presentation of general formula Ti100-a-b Cra Xb, however X is at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and it is attained by the hydrogen storing metal alloy which is expressed with 40<=a<=70 and 0< b<=20, and is characterized by the crystal structure being body-centered cubic structure (BCC mold). moreover, the above-mentioned purpose be attain also by the manufacture approach of the hydrogen storing metal alloy characterize by make as [have / the crystal structure / in ordinary temperature / body-centered cubic structure (BCC mold)] by hold said alloy after the dissolution / casting, hold said ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, TiCr2 except for a single phase field), and carry out quenching processing after that.

[0008]

[Embodiment of the Invention] As an example of the alloy of this invention, the range of a Ti-Cr-Mo system alloy is shown in drawing 1 . this 3 yuan state diagram -- TiCr2 of a Ti-Cr system it is -- the single phase field of a Laves phase exists and let this invention be the range where this range is avoided and the crystal structure consists of BCC. That is, it considers as the presentation including a segment top other than AD by within the limits [it was surrounded by the points A (Ti30Cr70) and B (Ti10Cr 70X20) of drawing 1 , and the segment which consists of C (Ti40Cr 40X20) and D (Ti60Cr40)].

[0009] On the other hand, with the alloy regularly disassembled into the detailed two phase of nano order by spinodal decomposition in the interior also in the BCC alloy in the old this invention person's etc. knowledge, a hydrogen desorption property is improved remarkably. the duality used as the base of this ternary alloy -- it is a system state diagram and it turns out especially by the Ti-Cr system, the Cr-Mo system, and the Cr-W system that the field of two-phase separation exists. The dual state diagram of a Ti-Cr system is shown in drawing 6 as an example. In this drawing, it is TiCr2. There is the solidus line of the two-phase separation which connects 1370 degrees C and an eutectoid point, and it is a homogeneity BCC phase at the temperature beyond this. In such a state diagram, the two phase from which the lattice constant which was formed of spinodal decomposition and grew up to be specific crystal orientation differs will have periodic structure at intervals of 1.0 to 100nm.

[0010] According to this regular nano order period structure, the big hydrogen storage capacity which a BCC alloy has structurally can be made to be able to emit in practical temperature and a pressure region, and activation conditions can be eased, and a reaction rate can be improved. On the other hand, it is TiCr2 of drawing 5 that the existence region of the BCC homogeneity phase in the alloy system of this invention was shown more concretely. It is the pseudo-binary diagram which set Mo as the third element, and/or W to X. The heat treatment temperature of this invention is the part 2 displayed with a slash, i.e., said TiCr, in this drawing. A single phase field is excepted and let BCC be the range which it has and can be come to homogeneity to a room temperature.

[0011] As mentioned above, this invention enables offer of the conventional BCC mold hydrogen storing metal alloy and the alloy which has the hydrogen absorption/emission ability of this level, without using expensive V. Furthermore, low cost-ization by optimization of a production process is also enabled. Next, an alloy presentation and heat treatment conditions of this invention are explained. Since the alloy presentation of this invention uses Ti, Cr, Mo, and/or W as a component, as compared with the hydrogen storing metal alloy which used the conventional V etc., it is the component which reduced cost and permuted V etc. by Mo and/or W, and the solution treatment range in a state diagram is expanded, therefore phase separation fully happens, and the alloy which was excellent in the hydrogen absorption/emission property with the two phase condition is obtained. Hereafter, the reason for component limitation of this invention is explained. General formula Ti100-a-b Cra Xb, however X are atomic % displays, and are expressed with 40<=a<=70 and 0< b<=20 by the inside a and b of Mo and/or W, and a formula. Said presentation range optimizes equalization of a BCC phase, and distortion of the crystal structure in the two-phase separation condition in the alloy by heat treatment, and can call them the optimal presentation which the detailed organization which enables promotion of the mobility of the hydrogen as a hydrogen storing metal alloy can do.

[0012] That is, the equilibrium pressure force [in / less than / 40at% / in Cr / the hydrogen absorption/emission property (pressure presentation constant-temperature-line-CT diagram) of a hydrogen storing metal alloy] is low, and it becomes difficult to take out again the hydrogen which carried out occlusion in ordinary temperature. Moreover, as for Cr, at 70at% **, said equilibrium pressure force has few hydrogen storage capacities in high 11 ordinary temperature. Furthermore, an alloy is not BCC-ized even if Mo and/or W heat-treat at 0at%. Since a hydrogen storage capacity falls, it becomes moreover, less practical in 20at% **. For this reason, it limited to the above-mentioned presentation range. Mo and/or the desirable range of W are 20% or less 5% or more. Moreover, the desirable range of Cr is 70% or less

50% or more.

[0013] By this invention, the BCC phase appeared said alloy in homogeneity, and the heat treatment conditions as the manufacture approach were specified so that the amount of hydrogen absorption/emission might be made into max. That is, it is characterized by BCC-izing an alloy by holding a hardener after the dissolution / casting, holding said ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, TiCr2 except for a single phase field), and carrying out quenching processing in an oil or iced water after that. That is, as heat treatment conditions for this invention, a high capacity hydrogen storage capacity BCC phase will exist in stability only in 1200 degrees C or more in the alloy of the above-mentioned presentation range. On the other hand, the alloy by which melting was carried out with the induction-heating method, the arc solution process, etc. usually metamorphoses into more stable C14 Laves phase below 1200 degrees C at the time of cooling. for this reason -- in order to form a BCC phase by the above-mentioned presentation -- an elevated temperature -- it is necessary to freeze a stable BCC phase to ordinary temperature

[0014]

[Example] The sample of a hydrogen storing metal alloy was created as follows as an example of this invention. A presentation is **Ti27Cr66Mo7 shown in drawing 1 (b), **Ti30Cr63Mo7, **Ti33Cr60Mo7, **Ti36Cr57Mo7, and **Ti39Cr54Mo7 as the range of this invention, i.e., presentation range in ABCD of drawing 1 (a). The quality governing was carried out. About 20g ingot performed all samples by the arc dissolution in an argon which used water-cooled copper Haas. After heating at 1400 degrees C after casting for 2 hours, heat treatment which carry out water cooling be perform, an organization be set to BCC, this ingot be grind in air, and all the data of this example be 60 degrees C and 10-4torr vacuum suction +50atm as activation. After carrying out the four cycle loop of the hydrogen pressurization and performing it, the hydrogen storage capacity and hydrogen absorption/emission property of an alloy be perform with the PCT measurement based on the vacuum condition specify for the pressure presentation constant-temperature line measuring method (JIS H7201) by the constant volume method.

[0015] Moreover, structural analysis of an alloy was performed using EDX (energy dispersion mold X diffraction) of a transmission electron microscope and attachment. The crystal structure model was created based on the information furthermore acquired with the transmission electron microscope, and lied belt analysis of powder X diffraction data was performed. Lied belt analysis can be asked for the weight fraction of each phase by count while it can carry out elaboration of the crystal structure parameter using diffraction reinforcement unlike the usual X-ray diffraction method. The analysis software RIETAN94 which Dr. National Institute for Research in Inorganic Materials Izumi developed was used for lied belt analysis.

[0016] Drawing 2 is drawing showing 0-degree C the hydrogen absorption and the emission process about the sample of the aforementioned [of this example] ** - **. In this drawing, it is **Ti27Cr66Mo7. And **Ti30Cr63Mo7 A hydrogen storage capacity hardly emits small. ** Ti33Cr60Mo7 And **Ti36Cr57Mo7 A hydrogen storage capacity is then improved and it is **Ti33Cr60Mo7. The Prato equilibrium pressure is about 1 MPa. Near and **Ti36Cr57Mo7 It is 1MPa then. It is the following, and occlusion and emission show the greatest value and shows the good value also in the Prato surface smoothness. Moreover, **Ti39Cr54Mo7 If it attaches, a hydrogen storage capacity is small and the hardly emitted inclination is shown. drawing 3 -- aforementioned **Ti39Cr54Mo7 ******** -- the hydrogen absorption property in 0 degree C and 40 degrees C is shown. In this component, the hydrogen storage capacity and the burst size have been improved in 40 degrees C, and the surface smoothness in plateau pressure is also a quite good result, and this component system found that it was promising practically.

[0017] The pressure (Prato equilibrium pressure) of the flat field of the pressure presentation constant-temperature line changes with the presentation ratios of Ti/Cr, as shown in drawing 8 (a) and (b). This drawing fixes Mo of a Ti-Cr-Mo system to 7at(s)%, and changes the amount of Ti and Cr. They are 0.01MPa(s) at the alloy presentation which shows the absorption pressure of 10 or less MPas by this invention at -40 degrees C considered as an operating environment of applications, such as a hydrogen tank and heat pump, and 100 degrees C. The alloy presentation which shows the above desorption pressure was made into the generic claim.

[0018] Moreover, the hydrogen absorption and the emission process (PCT property) of a sample which heat treatment of water quenching was performed to drawing 4 after 2-hour maintenance at 1400 degrees C after the arc dissolution like the above about Ti41Cr56 W3 are shown. In this drawing, the maximum hydrogen storage capacity in 40 degrees C shows about 2.3 Wt(s)%, and shows an about 2.4 Wt(s)% good value at 0 degree C, and 40 degrees C shows the result also with the quite good surface smoothness in plateau pressure also in the emission characteristic. Drawing 3 and drawing 4 are the hydrogen absorption properties of abbreviation identitas, and from this, by W, since it is twice [about] the atomic weight of this as compared with Mo, an addition is considered that BCC-ized effectiveness is because it is fully obtained at least. The comparison of the hydrogen absorption/emission ability of this invention material and comparison material is shown in Table 1.

[0019]

[Table 1]

試料	組成	水素吸蔵量(cc/g)	水素放出量(cc/g)
発明材	$Ti_{33}Cr_{60}Mo_7$	598	423
	$Ti_{36}Cr_{57}Mo_7$	674	502
比較材	$Ti_{20}Cr_{73}Mo_7$	146	40

[0020] From this table, it is Ti33Cr60Mo7 of this invention. A burst size is 598 cc/g in 598 cc/g then, and a hydrogen storage capacity is Ti36Cr57Mo7. A hydrogen storage capacity is 674 cc/g then, and the burst size shows 502 cc/g and a good value. On the other hand, at Ti20Cr73Mo7 of comparison material, as for the burst size, the hydrogen storage capacity shows the quite small value by 146 cc/g as compared with 40 cc/g and said this invention material. Clearly, this invention material has more available hydrogen movement magnitude than the Ra Beth alloy, is excellent in a hydrogen absorption/emission property, and is the BCC alloy and this level containing V of the former [characteristic value / the]. moreover, the table 2 -- presentation **Ti36Cr57Mo7 ******** -- a comparison shows the phase molar fraction of the BCC and the Laves phase by XRD after a hardener and heat treatment.

[0021] The chart of the X-ray relative intensity of XRD (Cu electrode, output 48kv) about Ti41Cr56 W3 and whenever [angle-of-diffraction] is shown in drawing 7 (a) and (b). (a) Drawing is a sample immediately after the arc dissolution, and the (b) Fig. is a result about heat treatment material (1400 degrees C -> water cooling). Although the phase existed in addition to this with the Laves phase immediately after the arc dissolution, it turns out that it is BCC homogeneity single phase by heat treatment.

[0022]

[Table 2]

	BCC	ラーベス
母合金	0	100
1300℃×2hr-油冷	86	14

[0023] The alloy heat-treated from this to a hardener being the Ra Beth single phase is understood that it has BCC-ized notably.

[0024]

[Effect of the Invention] By this invention, manufacture of the BCC mold hydrogen storing metal alloy with which a hydrogen absorption/emission property contains the conventional V etc. and which is the same level as an alloy is attained, without including expensive V etc. Moreover, drastic reduction of alloy raw material expense can be aimed at. Therefore, by this invention, a high capacity BCC mold hydrogen storing metal alloy can be extremely manufactured by low cost, and the utilization to various applications is attained.

[Translation done.]